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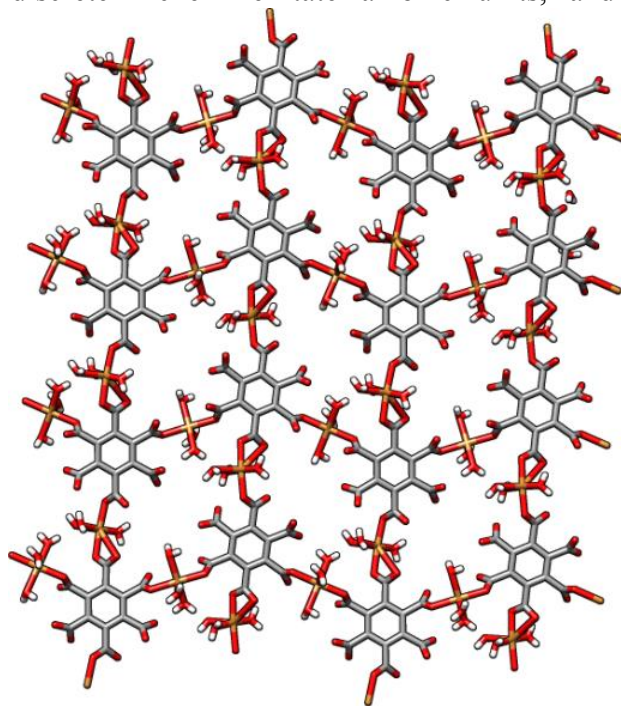
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# Structural variation in mellitate complexes of first-row transition metals: what chance for design?

William Clegg\* and James M. Holcroft†

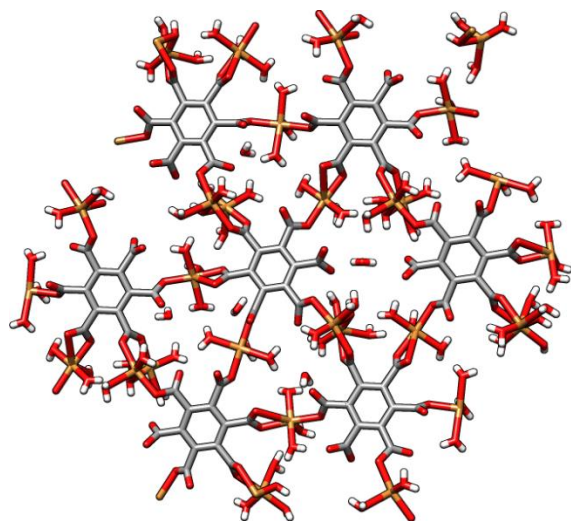
School of Chemistry, Newcastle University, Newcastle upon Tyne NE1 7RU, UK

Eight compounds of Co, Ni and Cu with mellitate ligands display a wide variety of structures with metal–mellitate coordination polymer dimensionality 0–3. Usually mellitate is fully deprotonated ( $\text{mel}^{6-}$ ), but there is one example of  $\text{Hmel}^{5-}$  and one of  $\text{H}_2\text{mel}^{4-}$ .  $[\text{M}_3(\text{mel})(\text{OH}_2)_{12}] \cdot 6\text{H}_2\text{O}$  ( $\text{M} = \text{Co}$  or  $\text{Ni}$ ) are chain polymers with octahedral  $\text{M}$ , while  $[\text{Cu}_7(\text{OH}_2)_{19}(\text{OH})_2(\text{mel})_2] \cdot 9\text{H}_2\text{O}$  has a 2D polymer sheet structure with square-based pyramidal  $\text{Cu}$ . Addition of  $\text{KOH}$  produces different compounds. Two incorporate  $\text{K}^+$  in the structures:  $\text{K}^+_2(\text{OH}_2)_5[\{\text{Ni}(\text{OH}_2)_5\}_2(\text{mel})]^{2-} \cdot 2\text{H}_2\text{O}$  contains discrete nickel–mellitate anionic units, and  $\text{K}^+_2(\text{OH}_2)_6[\{\text{Cu}(\text{OH}_2)_3\}_2(\text{mel})]^{2-} \cdot \text{H}_2\text{O}$  has a copper–mellitate 2D polymeric anion. For Co the product is  $[\text{Co}(\text{OH}_2)_6]^{2+}[\{\text{Co}(\text{OH}_2)_4\}_5(\text{mel})_2]^{2-} \cdot 4\text{H}_2\text{O}$ , with a 2D polymeric anion and discrete cations. A gel-supported synthesis leads to  $[\text{Cu}_3(\text{OH}_2)_{10}(\text{Hmel})][\text{Cu}_2(\text{OH}_2)_6(\text{Hmel})] \cdot 7\text{H}_2\text{O}$ , with two different copper–mellitate polymeric sheets arranged alternately in a stack.  $[\{\text{Cu}(\text{OH}_2)(\text{EtOH})(4,4'\text{-bipy})\}_2(\text{H}_2\text{mel})]$  contains a 3D copper–mellitate network with hexagonal channels, occupied by 4,4'-bipyridyl molecules coordinated to  $\text{Cu}$  at one end and hydrogen bonded to  $\text{H}_2\text{mel}^{4-}$  at the other. While some of these features are familiar from other structures, some are new, raising the question of how far design principles can be applied to the synthesis of mellitate complexes.



Professor William Clegg  
School of Chemistry  
Newcastle University  
Newcastle upon Tyne  
NE1 7RU, UK  
tel. +44 191 208 6649  
fax. +44 191 208 6929  
[bill.clegg@ncl.ac.uk](mailto:bill.clegg@ncl.ac.uk)

## For Table of Contents Use Only



First-row transition metal mellitate complexes display an intriguing variety of structures with a range of coordination polymer dimensionalities. The flexibility of coordinating behavior and the potential incomplete deprotonation of mellitic acid defy rational design of its complexes.

# Structural variation in mellitate complexes of first-row transition metals: what chance for design?

*William Clegg\* and James M. Holcroft†*

School of Chemistry, Newcastle University, Newcastle upon Tyne NE1 7RU, UK

## ABSTRACT

Eight compounds of Co, Ni and Cu with mellitate ligands display a wide variety of structures with metal–mellitate coordination polymer dimensionality 0–3. Usually mellitate is fully deprotonated ( $\text{mel}^{6-}$ ), but there is one example of  $\text{Hmel}^{5-}$  and one of  $\text{H}_2\text{mel}^{4-}$ .  $[\text{M}_3(\text{mel})(\text{OH}_2)_{12}] \cdot 6\text{H}_2\text{O}$  ( $\text{M} = \text{Co}$  or  $\text{Ni}$ ) are chain polymers with octahedral  $\text{M}$ , while  $[\text{Cu}_7(\text{OH}_2)_{19}(\text{OH})_2(\text{mel})_2] \cdot 9\text{H}_2\text{O}$  has a 2D polymer sheet structure with square-based pyramidal  $\text{Cu}$ . Addition of  $\text{KOH}$  produces different compounds. Two incorporate  $\text{K}^+$  in the structures:  $\text{K}^+_2(\text{OH}_2)_5[\{\text{Ni}(\text{OH}_2)_5\}_2(\text{mel})]^{2-} \cdot 2\text{H}_2\text{O}$  contains discrete nickel–mellitate anionic units, and  $\text{K}^+_2(\text{OH}_2)_6[\{\text{Cu}(\text{OH}_2)_3\}_2(\text{mel})]^{2-} \cdot \text{H}_2\text{O}$  has a copper–mellitate 2D polymeric anion. For  $\text{Co}$  the product is  $[\text{Co}(\text{OH}_2)_6]^{2+}[\{\text{Co}(\text{OH}_2)_4\}_5(\text{mel})_2]^{2-} \cdot 4\text{H}_2\text{O}$ , with a 2D polymeric anion and discrete cations. A gel-supported synthesis leads to  $[\text{Cu}_3(\text{OH}_2)_{10}(\text{Hmel})][\text{Cu}_2(\text{OH}_2)_6(\text{Hmel})] \cdot 7\text{H}_2\text{O}$ , with two different copper–mellitate polymeric sheets arranged alternately in a stack.  $[\{\text{Cu}(\text{OH}_2)(\text{EtOH})(4,4'\text{-bipy})\}_2(\text{H}_2\text{mel})]$  contains a 3D copper–mellitate network with hexagonal channels, occupied by 4,4'-bipyridyl molecules coordinated to  $\text{Cu}$  at one end and hydrogen bonded to  $\text{H}_2\text{mel}^{4-}$  at the other. While some of these features are familiar from other structures,

some are new, raising the question of how far design principles can be applied to the synthesis of mellitate complexes

## INTRODUCTION

Aromatic polycarboxylic acids are attractive candidates as ligands for the construction of polymeric metal coordination compounds including metal-organic frameworks (porous or otherwise) for a number of reasons. Benzene polycarboxylates offer a combination of rigidity of the aromatic ring with a degree of flexibility in orientation of the individually planar carboxylate substituents, restricted by steric interaction when two or more carboxylates are attached to adjacent ring C atoms, preventing coplanarity. Deprotonation can occur at one or more of the carboxylic acid groups, providing a range of anionic ligands to balance the charge of metal cations, in contrast to uncharged polyamines as ligands. Acid groups retaining their proton usually serve as hydrogen-bond donors, while both uncharged and deprotonated groups can act as hydrogen-bond acceptors. Deprotonated carboxylate groups function as ligand donors in a variety of ways ranging from simple monodentate to chelating and bridging, potentially binding several metal centers. These desirable characteristics are available, not only in benzene polycarboxylic acids themselves, but also in more complex ligands such as carboxylates of polyaromatics and heterocycles in combination with other potential ligand donor sites and functionalities.

Apart from benzoic acid, with only one carboxylate group, there are 11 benzene polycarboxylic acids having 2–6 acid groups and no other substituents. Of these, the most symmetrically substituted 1,3,5-tri- and 1,2,4,5-tetracarboxylic acids (trimesic acid and pyromellitic acid, respectively) along with the three dicarboxylic acids (phthalic, isophthalic, and especially

terephthalic) have been most widely used as multidentate ligands in metal complexes; they and expanded versions of them with more than one benzene ring have been key ligands in the development of isorecticular families of porous metal-organic frameworks.<sup>1</sup> The number of entries in the Cambridge Structural Database (CSD, Version 5.35 with updates to February 2014)<sup>2,3</sup> for metal complexes, salts and ester derivatives of each isomer (with no other substituents on the benzene ring) is shown in Table 1.

**Table 1.** CSD entries for complexes, salts and derivatives of benzene polycarboxylates

Common name	Carboxylic groups	Substituent positions	CSD entries
Mellitic	6	123456	100
	5	12345	14
Prehnitic	4	1234	21
Mellophanic	4	1235	2
Pyromellitic	4	1245	840
Hemimellitic	3	123	78
Trimellitic	3	124	130
Trimesic	3	135	1320
Phthalic	2	12	859
Isophthalic	2	13	952
Terephthalic	2	14	1954
Benzoic	1	1	3672

Mellitic acid, benzene-1,2,3,4,5,6-hexacarboxylic acid, stands out as exceptional in this table, in having far fewer entries than the other high-symmetry substituted polycarboxylic acids, with only about 10% of the numbers found for pyromellitic, trimesic and terephthalic acids.

Contributory factors to this shortage of known structures may include the high commercial cost and limited industrial usage of the acid compared with the less-substituted members of the family, though mellitic acid is of geochemical and environmental interest as the end-product of oxidation of graphite, coals and other forms of carbon.<sup>4</sup>

We have undertaken studies of the behavior of anions of mellitic acid as ligands in metal complexes as part of a research program in metal-organic frameworks using polycarboxylates, with transition metals, main group metals, and lanthanides, and we present here results for first-row transition metals (Co, Ni, and Cu); of the 100 CSD entries indicated in Table 1, 24 are complexes in which mellitate anions coordinate first-row transition metals, and all of these are complexes of the four metals Mn, Co, Ni, and Cu, some of them incorporating also alkali metal cations. Coordination polymers of this type are often obtained in microcrystalline form with little prospect of recrystallization when conventional solution-based synthesis methods are used, so we have used a range of techniques involving slow diffusion of reagent solutions, including simple layering of solutions and diffusion into silica gels impregnated with reagents. Usually products form as crystals over a period of days or weeks, and in some cases the amount of product is very small.

## EXPERIMENTAL SECTION

**Materials and Physical Measurements.** All experiments were carried out in air. Transition metal salts, mellitic acid, potassium and sodium hydroxides, 4,4'-bipyridyl, and methanol were commercial samples and were used without further purification. Water was distilled for use as a solvent. Elemental analysis was carried out by the Newcastle University chemical analytical service using a Carlo Erba 1108 Elemental Analyser. Powder X-ray diffraction measurements

were made with Cu- $K\alpha$  radiation at room temperature on a PANalytical X'Pert Pro Diffractometer fitted with an X'Celerator multiple-strip detector and secondary monochromator, in continuous measurement mode over a  $2\theta$  range of 5–120°.

**Synthesis of transition metal mellitate complexes.** Complexes were prepared by slow liquid diffusion of solutions of reagents. In most cases, 2 ml of a solution of the metal salt (0.33 mmol dissolved in 10 ml water) was carefully layered over 2 ml of a solution of mellitic acid (0.058 g, 0.17 mmol in 10 ml water) in a small glass vial, which was covered and left undisturbed for several days or weeks until crystals formed. The metal salts used were  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , and  $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ . For compounds **2**, **4**, and **6** the mellitic acid solution contained also potassium hydroxide (0.336 g, 6 mmol in 10 ml). For compound **7**,  $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (0.079 g, 0.33 mmol) in water (10 ml) and mellitic acid (0.058 g, 0.17 mmol) in water (10 ml) were placed on top of a 5% tetramethoxysilane gel containing sodium hydroxide (0.159 g, 4 mmol) in a sample tube. Diffusion of the solvents into the gel gave a few blue crystals after 3 weeks. For compound **8**, 1 ml of a methanol solution of  $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (0.08 g, 0.33 mmol in 10 ml) was placed in the bottom of one vertical tube of an H-shaped liquid diffusion vessel, and 1 ml of a methanol solution of mellitic acid (0.058 g, 0.17 mmol in 10 ml) was placed together with 1 ml of a methanol solution of 4,4'-bipyridyl (0.027 g, 0.17 mmol in 10 ml) in the other vertical tube; water was added to connect the solutions via the horizontal tube, and the apparatus was left undisturbed for 4 weeks until a few crystals were formed. In each case, crystals suitable for X-ray diffraction were obtained from the synthesis without further recrystallization.



**Chemical analysis.** **2**: calcd (%) for  $C_{24}H_{60}Co_6O_{54}$ : C 18.4, H 3.8; found: C 18.5, H 4.2. **3**: calcd (%) for  $C_{12}H_{36}Ni_3O_{30}$ : C 17.2, H 4.3; found: C 17.2, H 4.5. **4**: calcd (%) for  $C_{12}H_{34}K_2Ni_2O_{29}$ : C 17.2, H 4.1; found: C 17.7, H 3.8.

**X-ray Crystallography.** For compounds **1–5** and **7** data were collected on an Agilent Technologies Gemini A Ultra diffractometer at 150 K, using  $CuK\alpha$  radiation ( $\lambda = 1.54184 \text{ \AA}$ ) for **2** and  $MoK\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) otherwise. Data for compound **6** were collected with synchrotron radiation ( $\lambda = 0.7749 \text{ \AA}$ ) at Beamline 11.3.1 of the Advanced Light Source (Bruker APEX2 diffractometer); beamline I19 of Diamond Light Source ( $\lambda = 0.6689 \text{ \AA}$ , Crystal Logics diffractometer with Rigaku Saturn 724+ detector) was used to collect data for compound **8**, also at 150 K in both cases. Semi-empirical corrections for absorption, incident beam variations and frame scaling were based on symmetry-equivalent and repeated reflections (Agilent CrysAlisPro and Bruker SADABS software). The crystal structures were solved by direct methods and refined on all unique  $F^2$  values using SHELXTL and SHELXL-2014 programs. H atom positions were assigned from difference maps and/or on the basis of hydrogen bonding patterns as indicated by appropriate and consistent O...O and O...N contacts. O–H distances for water molecules were restrained to be equal, as were H...H distances in order to give suitable H–O–H angles. For most of the structures, restraints were also applied to the displacement parameters of the C and O atoms of the mellitate ligands, and isotropic displacement parameters of H atoms were constrained to 1.2 or 1.5 times the equivalent isotropic values of the O atoms. H atoms were not included for two of the uncoordinated water molecules in compound **7** (these have relatively large displacement parameters and may be subject to unresolved minor disorder), for the methanol ligand in compound **8**, and for the minor component of a disordered water molecule in compound **6** (one potassium ion is also disordered and the disordered water molecule is

bonded to it). A minor twin component was identified in the structure of compound **4**, contributing less than 2% of the diffraction, and was included in the refinement model. Selected crystallographic information is provided in Table 2, with full details in the Supporting Information. Programs were standard commercial data collection software,<sup>5,6,7</sup> SHELXTL version 5 for structure solution,<sup>8</sup> SHELXL-2014 for refinement,<sup>9</sup> and SHELXTL and Chimera<sup>10</sup> for graphical display of structures.

**Table 2.** Crystallographic Information

compound	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
chem form	$\text{C}_{12}\text{H}_{24}\text{Co}_3\text{O}_{24}\cdot 6\text{H}_2\text{O}$	$\text{H}_{12}\text{CoO}_6^{2+}\cdot \text{C}_{24}\text{H}_{40}\text{Co}_5\text{O}_{44}^{2-}\cdot 4\text{H}_2\text{O}$	$\text{C}_{12}\text{H}_{24}\text{Ni}_3\text{O}_{24}\cdot 6\text{H}_2\text{O}$	$2\text{K}^+\cdot \text{C}_{12}\text{H}_{20}\text{Ni}_2\text{O}_{22}^{2-}\cdot 7\text{H}_2\text{O}$
cryst syst	orthorhombic	triclinic	orthorhombic	monoclinic
space group	<i>Pbca</i>	$P\bar{1}$	<i>Pbca</i>	$P2_1/c$
<i>a</i> (Å)	17.0348(11)	8.7373(7)	16.9667(9)	6.7014(2)
<i>b</i> (Å)	8.4649(5)	9.7058(6)	8.4375(4)	19.2147(6)
<i>c</i> (Å)	20.0674(11)	15.3909(14)	19.9676(9)	23.0383(6)
$\alpha$ (deg)		84.254(6)		
$\beta$ (deg)		81.361(7)		92.119(3)
$\gamma$ (deg)		78.367(6)		
<i>V</i> (Å <sup>3</sup> )	2893.7(3)	1260.58(18)	2858.5(2)	2964.51(15)
<i>Z</i>	4	1	4	4
<i>D</i> <sub>calcd</sub> (g cm <sup>-3</sup> )	1.922	2.063	1.944	1.878
$\mu$ (mm <sup>-1</sup> )	1.82	16.42	2.08	1.67
reflns measd	11688	6776	9314	18233
unique reflns	3481	3862	2513	5224

$R_{\text{int}}$	0.0674	0.0518	0.0790	0.0533
transmission range	0.85–0.90	0.20–0.50	0.60–0.80	0.80–0.85
refined params	278	472	259	510
restraints	308	864	349	1021
$R(F, F^2 > 2\sigma)$	0.0398	0.0498	0.0437	0.0481
$R_w(F^2, \text{all data})$	0.0669	0.1273	0.0778	0.1199
GOF ( $F^2$ , all data)	0.986	0.983	1.007	1.000
final diff map	0.62, –0.48	0.98, –0.60	0.47, –0.43	1.33, –0.76
extremes ( $\text{e } \text{\AA}^{-3}$ )				

compound	<b>5</b>	<b>6</b>	<b>7</b>	<b>8</b>
chem form	$\text{C}_{24}\text{H}_{40}\text{Cu}_7\text{O}_{45} \cdot 9\text{H}_2\text{O}$	$2\text{K}^+ \cdot \text{C}_{12}\text{H}_{12}\text{Cu}_2\text{O}_{18}^{2-} \cdot 7\text{H}_2\text{O}$	$\text{C}_{24}\text{H}_{34}\text{Cu}_5\text{O}_{40} \cdot 7\text{H}_2\text{O}$	$\text{C}_{33}\text{H}_{26}\text{Cu}_2\text{N}_4\text{O}_{15}$
cryst syst	orthorhombic	orthorhombic	monoclinic	trigonal
space group	<i>Iba</i> 2	<i>Pbca</i>	<i>Cc</i>	<i>P</i> 3 <sub>1</sub> 21
$a$ (Å)	19.2600(4)	19.4561(10)	27.350(2)	10.136(3)
$b$ (Å)	21.0541(3)	12.5110(6)	9.5383(6)	
$c$ (Å)	12.8450(2)	21.4202(11)	18.5428(16)	26.725(7)
$\beta$ (deg)			113.005(10)	
$V$ (Å <sup>3</sup> )	5208.67(15)	5214.0(5)	4452.6(7)	2377.8(15)

<i>Z</i>	4	8	4	3
$D_{\text{calcd}}$ (g cm <sup>-3</sup> )	2.111	1.976	2.098	1.772
$\mu$ (mm <sup>-1</sup> )	2.94	2.52	2.49	1.27
reflns measd	10096	45524	12708	18414
unique reflns	4891	6453	6109	3901
$R_{\text{int}}$	0.0254	0.0727	0.0486	0.0494
transmission range	0.62–0.85	0.79–0.94	0.80–0.88	0.95–0.98
refined params	473	458	817	258
restraints	808	409	1330	1
$R$ ( $F$ , $F^2 > 2\sigma$ )	0.0230	0.0345	0.0376	0.0492
$R_w$ ( $F^2$ , all data)	0.0493	0.0952	0.0817	0.1449
GOF ( $F^2$ , all data)	0.978	1.077	1.020	1.065
absolute structure parameter	0.045(8)		0.015(16)	0.030(9)
final diff map	0.78, –0.38	0.71, –0.67	0.85, –0.49	0.64, –0.49
extremes (e Å <sup>-3</sup> )				

## RESULTS AND DISCUSSION

**Synthesis.** Two basic approaches were taken to the synthesis of complexes of late first-row transition metals with anions of mellitic acid. The simple one was direct reaction of a hydrated metal nitrate with mellitic acid itself ( $\text{H}_6\text{mel}$ ) in water, using slow liquid diffusion of the reagent solutions to prevent rapid formation of the product as a microcrystalline powder. A variant was the use of sodium or potassium hydroxide to promote the deprotonation of the mellitic acid; this was carried out both by simple liquid diffusion and by diffusion of reagents into a hydroxide-impregnated silica gel in which deprotonation and complex formation took place. The conditions employed were such that product formation occurred over a period of some weeks in most cases, enabling single crystals of reasonable size to be obtained, suitable for X-ray diffraction; for compounds **6** and **8**, however, the crystals were too weakly diffracting for successful conventional laboratory study and had to be investigated with synchrotron radiation.

Where possible with the availability of sufficient material, chemical and phase purity was confirmed by standard microanalysis and powder X-ray diffraction measurements; observed and calculated powder diffraction patterns are provided in the Supporting Information.

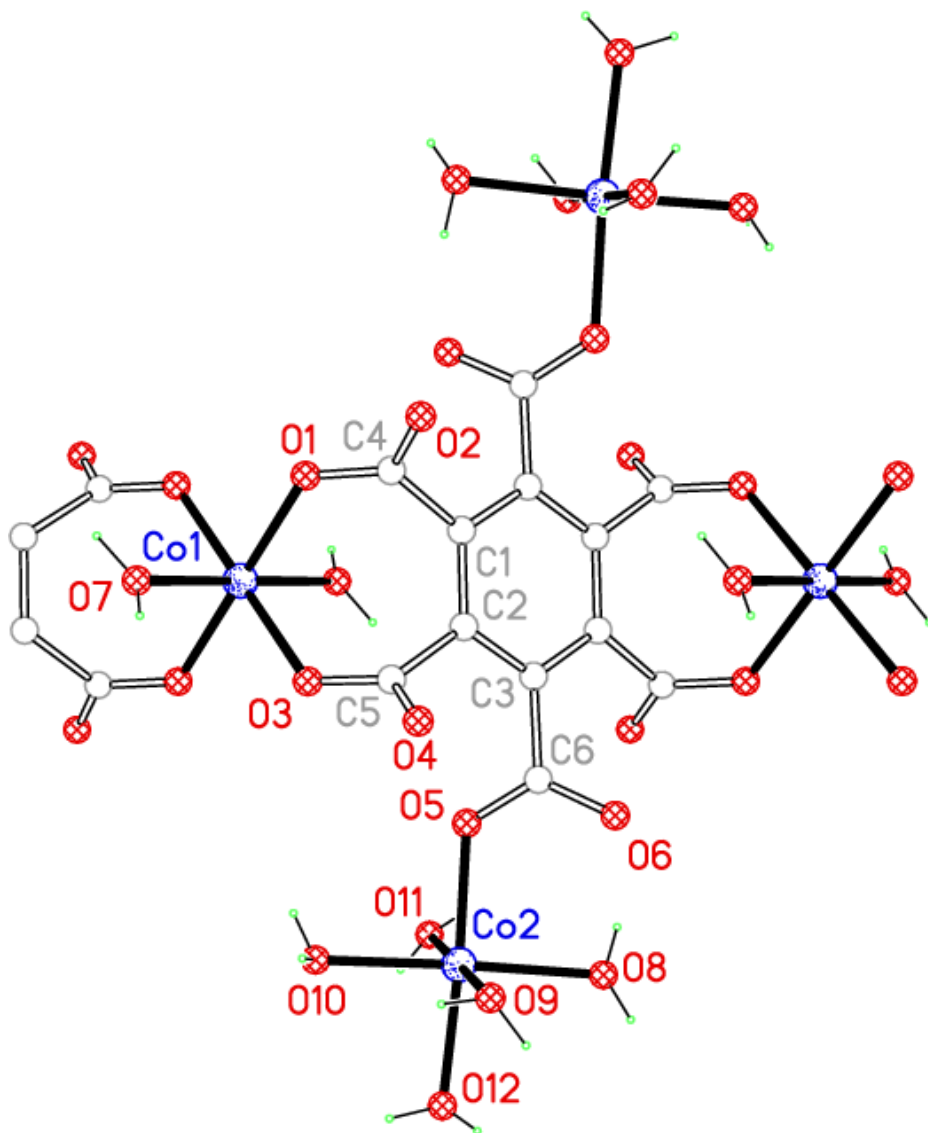
**Crystal structures.** All of the compounds except for **4** were found to be coordination polymers, with mellitate ligands acting as bridges between metal centers; the networks are variously 1-, 2- and 3-dimensional. Metal ions are coordinated in most of the structures by carboxylate groups and/or water molecules, and in most cases there are additional uncoordinated water molecules present, contributing to extensive hydrogen bonding. Compounds **1–6** all contain fully deprotonated mellitate ( $\text{mel}^{6-}$ ) anions; compound **7** contains  $\text{Hmel}^{5-}$ , and compound **8** contains  $\text{H}_2\text{mel}^{4-}$ , deprotonation in these cases being incomplete and the still-protonated acid groups

taking no part in metal coordination. Compounds **1**, **3** and **5**, prepared from metal salts and mellitic acid without the addition of sodium or potassium hydroxide, contain only transition metal cations, multidentate  $\text{mel}^{6-}$  ligands and both coordinated and uncoordinated water (but also hydroxide ligands in **5**); compounds **4** and **6**, synthesized in the presence of potassium hydroxide, incorporate potassium cations in their structures, which is not the case for the similarly prepared compound **2**, which is a salt with  $\text{Co}^{2+}$  in both the discrete cation and the polymeric anion. Compound **7** incorporates neither sodium nor hydroxide ions in its structure, which contains only  $\text{Cu}^{2+}$  ions,  $\text{Hmel}^{5-}$  ligands, and both coordinated and uncoordinated water molecules. Compound **8** additionally has 4,4'-bipyridyl and methanol as ligands.

**Compound 1.** The polymer repeat unit of compound **1** is formulated as  $[\text{Co}_3(\text{mel})(\text{OH}_2)_{12}] \cdot 6\text{H}_2\text{O}$  or, more explicitly, as  $[\{\text{Co}(\text{OH}_2)_5\}_2\{\text{Co}(\text{OH}_2)_2\}(\text{mel})] \cdot 6\text{H}_2\text{O}$ . The structure has been reported twice previously,<sup>11,12</sup> with analytical and DTA characterization, and our own results show no significant difference; they are included here for completeness of the series and for comparison with the other structures, especially as this compound is found to be isostructural with the nickel analogue, **3**. A triclinic polymorph is also known,<sup>13</sup> which has essentially the same coordination polymer chain structure but a different hydrogen-bonding arrangement linking the chains and uncoordinated water molecules together.

The structure of compound **1** may best be described as a metal-organic polymer chain (Figure 1) consisting of alternating  $\text{Co}^{2+}$  cations and  $\text{mel}^{6-}$  anions, each of these components lying on an inversion center; the metal center Co1 is chelated by two adjacent carboxylate groups of each of two ligands, and the ligand serves as a bis-chelate through its 1,2 and 4,5 substituents (O1 and O3). The square-planar coordination of Co1 generated in this way is augmented by two *trans*-aqua ligands O7 to complete the octahedral coordination. The two remaining, mutually *trans*,

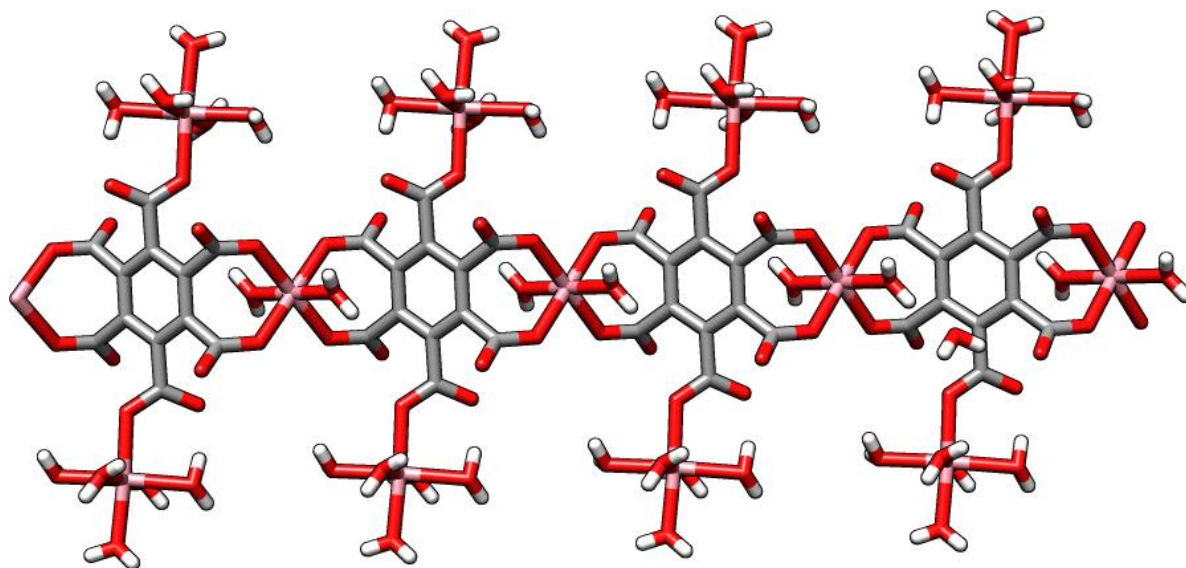
carboxylate groups of  $\text{mel}^{6-}$  form monodentate attachments to  $\text{Co}(\text{OH}_2)_5^{2+}$  ions (O5–Co2), which thus serve as terminal decorations on opposite sides of the polymer chain, with octahedral coordination of all metal centers.



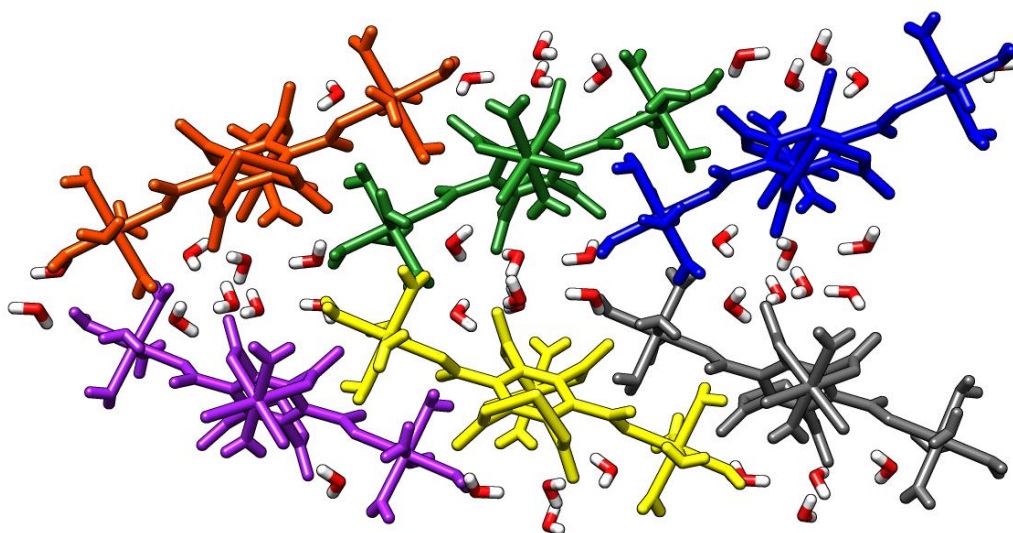
**Figure 1.** A section of the coordination polymer chain structure of compound **1** showing complete metal coordination, the environment of the mellitate ligand, and atom labels of the asymmetric unit. The chain runs horizontally across the page.



Because the carboxylate groups are twisted markedly out of the plane of the benzene ring by steric congestion of the hexa-substitution, the chelated metal ions lie above and below the ring plane, and so the chain (Figure 2) has a stepped shape. All the chains lie parallel to the crystallographic *b* axis. The spaces between the chains are occupied by uncoordinated water molecules, as shown in Figure 3. There is an extensive 3D hydrogen-bonding network with coordinated and uncoordinated water molecules acting as donors and acceptors, most of the carboxylate O atoms also being acceptors; details of hydrogen bonding are given in the Supporting Information.



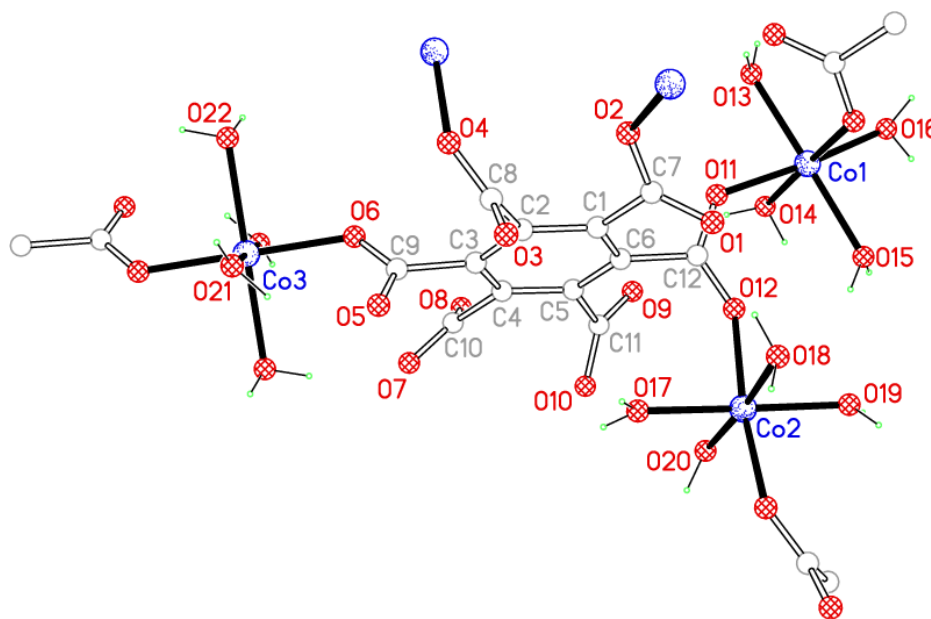
**Figure 2.** The stepped chain in the structure of compound **1**; 4 repeat units are shown. The view is approximately along the *a* axis, with *b* running horizontal.



**Figure 3.** The structure of compound **1** viewed along the *b* axis (the polymer chain direction), showing uncoordinated water molecules occupying spaces between the chains. Each of 6 chains is displayed in a different color. The *c* axis runs horizontal.

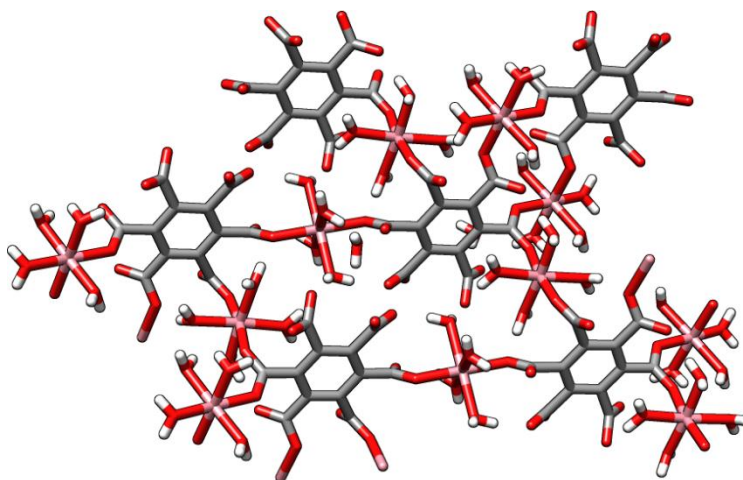
Three other previously reported  $\text{Co}^{2+}$  complexes of mellitate have formulae similar to that of compound **1**.<sup>14</sup>  $[\text{Co}_3(\text{mel})(\text{OH}_2)_5] \cdot \text{H}_2\text{O}$  and  $[\text{Co}_4(\text{mel})(\text{OH})_2(\text{OH}_2)_6] \cdot \text{H}_2\text{O}$  were prepared by hydrothermal synthesis using different  $\text{Co}^{2+}$  salts, mellitic acid, water, and nitrogen-donor additives that are not incorporated in the structures; the proportion of water in these structures is considerably lower (approximately 2:1 for water:metal) than in compound **1** (6:1), consistent with the synthetic method and resulting in structures with higher densities, a 3D coordination network, and less hydrogen bonding.  $[\text{Co}_3(\text{mel})(\text{OH}_2)_{14}] \cdot 2\text{MeOH} \cdot 6\text{H}_2\text{O}$  (in which there is some disorder of methanol and water in coordinating and uncoordinating sites, so this is a simplified formula), prepared by an ambient-pressure mixed-solvent method more like our own, has a Co:mellitate:water composition very similar to that of compound **1** and consists also of coordination polymer chains linked by hydrogen bonding.

**Compound 2.** Although the cobalt compound **2** was synthesized in the presence of potassium hydroxide, neither  $K^+$  nor  $OH^-$  ions are incorporated in the product structure, in contrast to the results for the nickel and copper compounds **4** and **6**. The ingredients of this structure are, once again as in compound **1**,  $Co^{2+}$  cations coordinated by water molecules and  $mel^{6-}$  anions, together with uncoordinated water molecules, but the details of the structure are quite different, resulting presumably from the different pH conditions. Here we have an ionic compound with discrete cobalt-centered cations and anionic coordination polymer sheets formulated as  $[Co(OH_2)_6]^{2+} [ \{Co(OH_2)_4\}_5(mel)_2 \}^{2-} \cdot 4H_2O$ . The cation is the well-known octahedral  $[Co(OH_2)_6]^{2+}$  lying on an inversion center and requires no further comment. The anion has a polymeric sheet structure; the asymmetric unit of which contains two  $Co^{2+}$  cations in general positions and one on an inversion center, one  $mel^{6-}$  anion, and ten coordinated water molecules, as shown in Figure 4.



**Figure 4.** The asymmetric unit of the anion of compound **2**, with additional symmetry-related atoms to complete the metal coordination of Co1–Co3 and the environment of the mellitate anion; non-H atoms of the asymmetric unit are labeled.

The mellitate anion coordinates to a total of 5 metal ions; two adjacent carboxylate groups (at C4 and C5) give no coordination. three (at C1, C2 and C3) are monodentate donors, and the other (at C6) uses both of its O atoms to coordinate to different  $\text{Co}^{2+}$  ions, thus acting as a bridging group with a *syn,anti* arrangement. Co1 and Co2 are each coordinated by four terminal aqua ligands and by two carboxylate groups of different mellitate anions, these ligands lying *cis* in the case of Co1 and *trans* in the case of Co2. Co3, lying on an inversion center, has a coordination environment similar to that of Co2, with two *trans* carboxylate groups and four coplanar aqua ligands. All aqua ligands, as in compound **1**, are terminal, and the polymeric structure is generated by the Co–mellitate coordination. In contrast to the neutral 1D polymer of compound **1**, here we have a 2D polymeric anion (Figure 5) balanced by discrete (0D) cations. Further, uncoordinated, water molecules engage with the aqua and mellitate ligands to give an extensive 3D hydrogen-bonding network, details of which are provided in the Supporting Information. We note that the Co:mellitate:water ratios of compounds **1** (3:1:18) and **2** (3:1:15) are almost the same.



**Figure 5.** Part of the polymeric sheet anion of compound **2**. The view direction is approximately along [011] with the *a* axis running diagonally from top left to bottom right.

Compound **2** has a number of similarities to the manganese mellitate complex  $[\text{Mn}(\text{OH}_2)_6]^{2+} [\{\text{Mn}(\text{OH}_2)_3\}_2(\text{mel})] \cdot 2\text{H}_2\text{O}$ , synthesized under broadly similar conditions, though there are some significant differences also.<sup>15,16</sup> The manganese compound has discrete octahedral cations and a sheet polymeric anion, but in the anion all metal centers are equivalent and are coordinated by three carboxylate groups and three water molecules in a *mer* arrangement; the mellitate ligand coordinates to 6 manganese centers and its benzene ring lies perpendicular to the anion sheet, whereas the mellitate ligands in compound **2** lie at an angle of almost 30° to the anion sheet.

**Compound 3.** This nickel compound was prepared in the same way as the corresponding cobalt compound **1** and it is found to be completely isostructural, even to the details of the hydrogen bonding; the two structures can be overlaid almost exactly, the most significant difference being a small shortening of the Ni–O bonds compared to Co–O, as is expected. The structural description given above applies equally well to this compound. Only two nickel mellitate structures have been reported previously (in contrast to nine for cobalt). One contains also oxamide oxime ligands, which block four of the six coordination sites at each nickel center, leading to a chain polymer structure with tetracoordinating  $\text{H}_2\text{mel}^{4-}$  ligands linked together by pairs of nickel ions; the mellitate retains two of its carboxylic acid H atoms in a *trans* arrangement, and water molecules are present only in uncoordinated form.<sup>17</sup> The other, from a hydrothermal synthesis, is formulated as  $[\text{Ni}_4(\text{mel})(\text{OH})_2(\text{OH}_2)_6]$  with a 2D polymeric structure in which each  $\text{mel}^{6-}$  ligand is attached to 8 different nickel ions (the three independent carboxylate groups bond to 1, 2 and 3 ions), there are  $\mu_3$ -OH groups, and there are no uncoordinated water molecules.

**Compound 4.** The reaction of a nickel(II) salt with mellitic acid in the presence of potassium hydroxide in aqueous solution leads to the incorporation of  $K^+$  (but not  $OH^-$ ) ions in the product, and to some structural features quite different from those of the compounds already described. The compound may be formulated as  $K^+_2(OH_2)_5[\{Ni(OH_2)_5\}_2(mel)]^{2-} \cdot 2H_2O$ , in which 10 molecules of water are coordinated to the two nickel ions (5 each), 5 to the potassium ions only, and 2 remain uncoordinated. Figure 6 shows the crystallographic asymmetric unit, to which have been added other symmetry-equivalent atoms sufficient to display the complete coordination environment of all the metal ions, mellitate ions and water molecules in the asymmetric unit. O13–O22 are water molecules coordinated to nickel, O23–O27 are coordinated to potassium, and O28 and O29 are not coordinated.

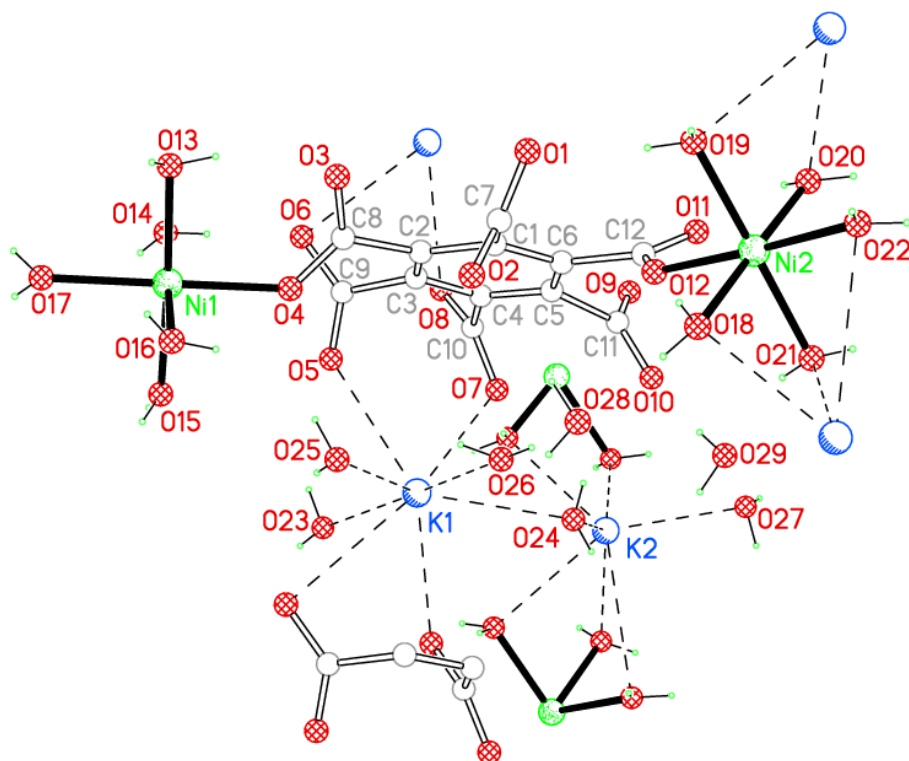


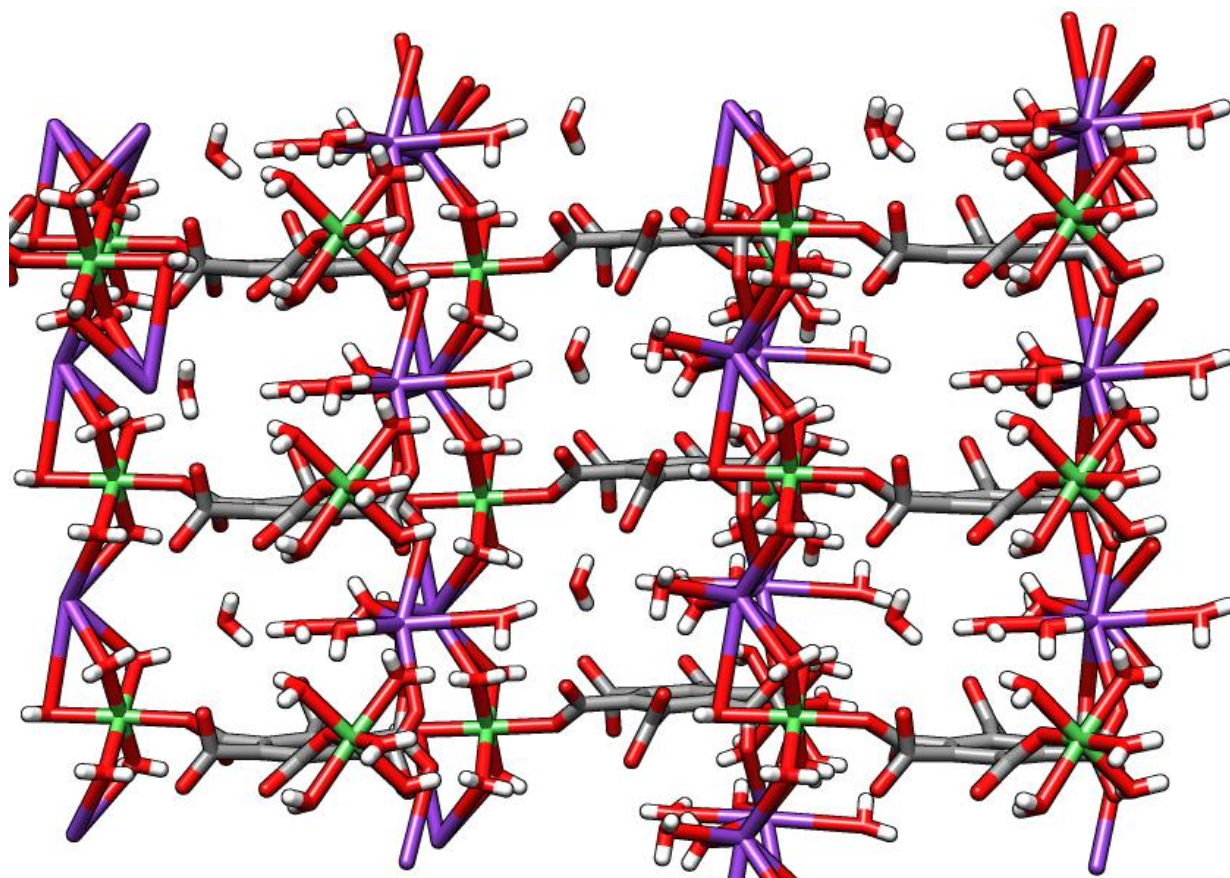
Figure 6. The asymmetric unit (with labeled atoms) and its coordination environment in the crystal structure of compound 4.

If only the nickel and mellitate ions are considered, together with aqua ligands on nickel, the structure contains discrete  $[\{\text{Ni}(\text{OH}_2)_5\}_2(\text{mel})]^{2-}$  units, which are not connected together to form any polymeric arrangement. The two nickel ions are coordinated by only one carboxylate group each, in a simple monodentate fashion, and have their octahedral coordination completed by 5 aqua ligands each. Only two of the six carboxylate groups bind to nickel ions.

The two potassium ions in the asymmetric unit have quite different environments and structural functions. K1 is coordinated by two carboxylate O atoms of one mellitate ion, and by the other two O atoms of the same carboxylate groups in another mellitate ion displaced one unit cell along the *a* axis; it thus serves to link the anionic units together in a chain along this axis. K1 is further coordinated by 4 water molecules, 3 of them terminally and O24 as a bridge between K1 and K2, giving a total coordination number of 8 for K1 in an irregular geometry. K2 is coordinated exclusively by 7 water molecules: 3 of these are aqua ligands on one symmetry-equivalent of Ni2, and 2 are aqua ligands on another equivalent of Ni2, these two metal ions being separated by one *a*-axis repeat, so that K2 also links anionic units along this axis; O24 bridges K2 and K1 as previously noted, and O27 is a terminal ligand for K2. For both K1 and K2 one of the K–O bonds (to carbonyl O for K1, to Ni-coordinated water for K2) is rather longer than the others. It may be noted that all the aqua ligands on Ni1 are terminal, and all of those on Ni2 serve as bridges between nickel and potassium ions.

The only coordinative connection between the *a*-axis chains is the bridging water molecule attached to both K1 and K2. This connection generates 2D sheets in the *ab* plane (Figure 7). Only hydrogen bonds link the sheets together to give a 2D network. Two of the six carboxylate groups of the fully deprotonated mellitate anion remain uncoordinated to either nickel or potassium.





**Figure 7.** The sheet structure of compound **4**, viewed along the  $c$  axis. The  $b$  axis runs horizontal.

Previously reported structures of mellitate complexes containing both a transition metal and an alkali metal have a considerably lower water content than compound **4** and all were synthesized hydrothermally. The isostructural family of six compounds  $M_2[M'_2(OH_2)_2(mel)]$  ( $M = K, Rb$ ;  $M' = Mn, Co, Ni$ ) have a 3D coordination network of transition metal and mellitate ions, even if the alkali metals are ignored, and the same is true for the compound  $(NH_4)_2[Co_2(OH_2)_2(mel)]$  in which the place of the alkali metal is taken by an ammonium ion.<sup>18</sup> This is also the case for  $[Li(OH_2)]_2[Mn_2(OH_2)_4(mel)]$  with a slightly higher water content, the lithium ions carrying a terminal aqua ligand each.<sup>19</sup> The structure of compound **4** is thus unprecedented in this respect.



Indeed, all previously reported structures in which mellitate serves as a ligand to any transition metal or lanthanide are polymeric in at least one dimension.

**Compound 5.** This Cu compound has a rather more complex structure than those of compounds **1** (Co) and **3** (Ni), which were prepared in the same way. Although no hydroxide was used in the synthesis,  $\text{OH}^-$  anions appear in the structure as bridging ligands between copper centers. Figure 8 shows the crystallographic asymmetric unit, to which have been added other symmetry-equivalent atoms sufficient to display the complete coordination environment of all the metal ions, mellitate and hydroxide ions, and water molecules in the asymmetric unit. O13–O23 are water molecules coordinated to copper (except that O15 is hydroxide), O24–O28 are not coordinated. The formula may be written  $[\text{Cu}_7(\text{OH}_2)_{19}(\text{OH})_2(\text{mel})_2] \cdot 9\text{H}_2\text{O}$ .

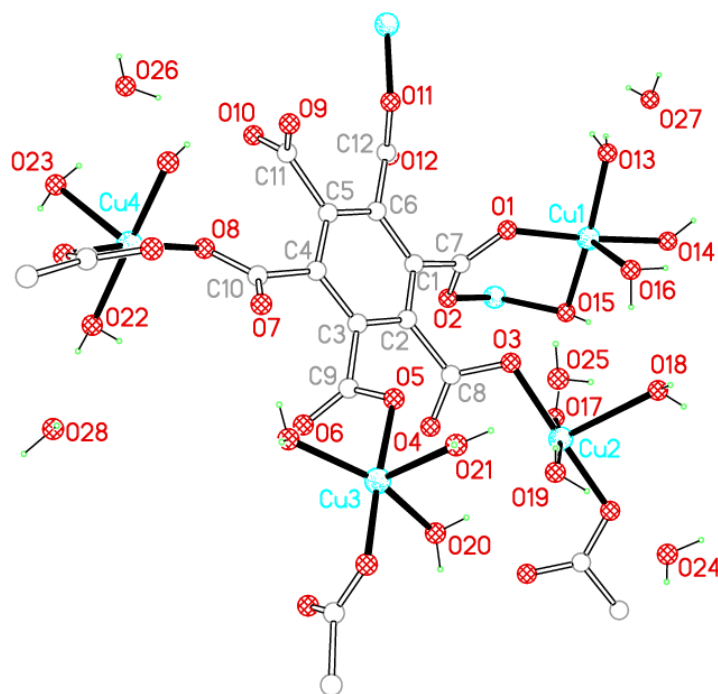


Figure 8. The asymmetric unit (with labeled atoms) and its coordination environment in the crystal structure of compound **5**.

All the copper ions are five-coordinate with a coordination geometry close to square-based pyramidal, an aqua ligand occupying the apical site in each case. Cu1 is coordinated by three aqua ligands, one carboxylate group, and a hydroxide ligand that forms a bridge to a symmetry-equivalent of Cu4. Cu2, which lies on a crystallographic twofold rotation axis, is coordinated by two carboxylate groups and three aqua ligands. Cu3 has a similar arrangement to Cu2, but it lies in a general position. Cu4 is coordinated by two carboxylates, two aqua ligands, and a hydroxide bridge. All aqua ligands in the structure are terminal, while the single hydroxide in the asymmetric unit bridges two copper ions.

Of the six carboxylate groups of the mellitate anion, four act as monodentate donors to copper ions, one (at C1) uses both of its O atoms to bridge two copper ions (which are also bridged by hydroxide), and one (at C5) remains uncoordinated, but is clearly deprotonated with two almost equal C–O bond lengths and two O atoms that serve as acceptors of three hydrogen bonds each. The copper and mellitate ions together generate a 2D sheet polymer structure (Figure 9), and the sheets are held together by hydrogen bonds, both directly between sheets and via uncoordinated water molecules (Figure 10).

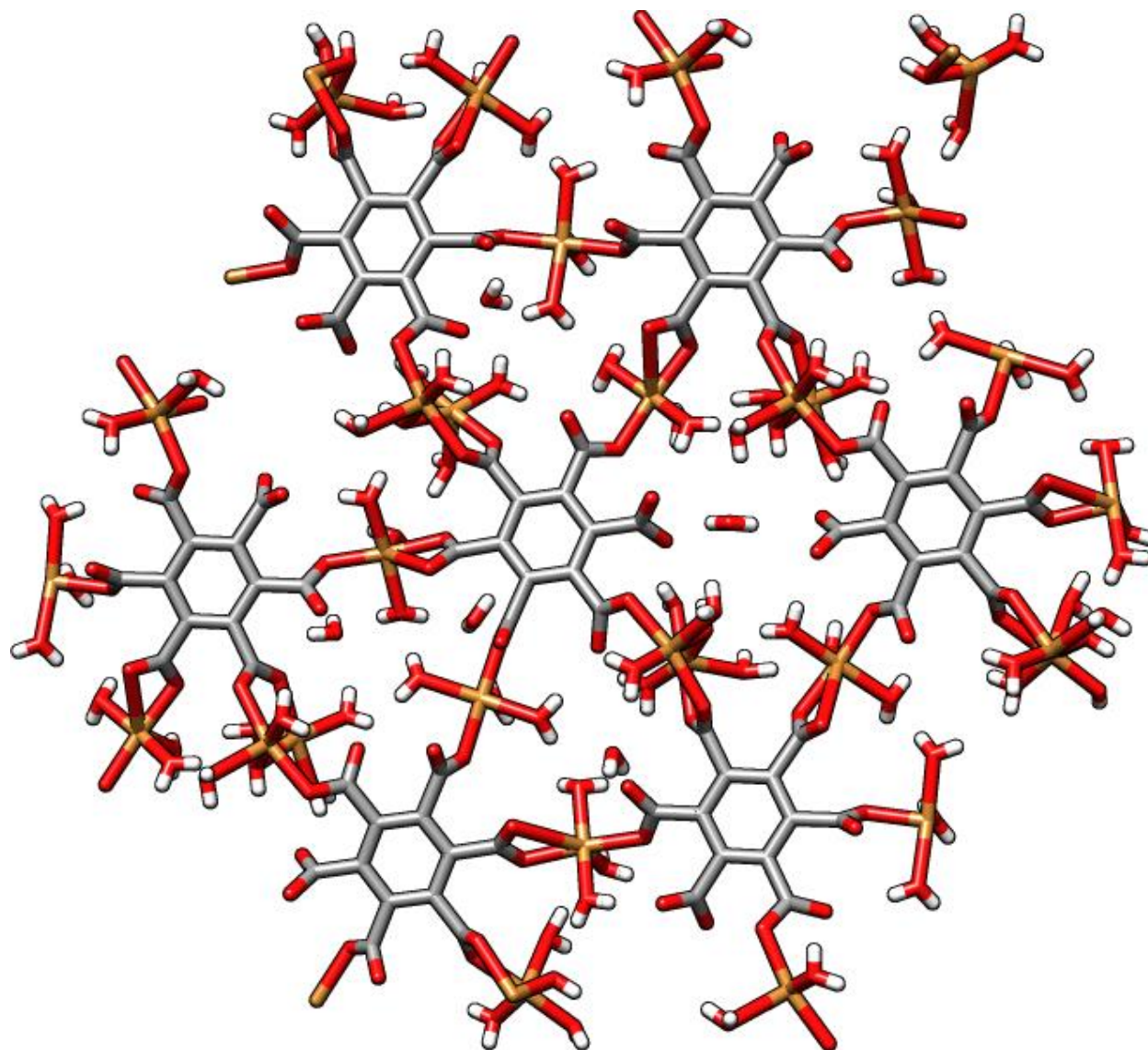


Figure 9. The sheet polymeric structure of compound **5**. The view is approximately along the  $c$  axis with the  $b$  axis running horizontal.

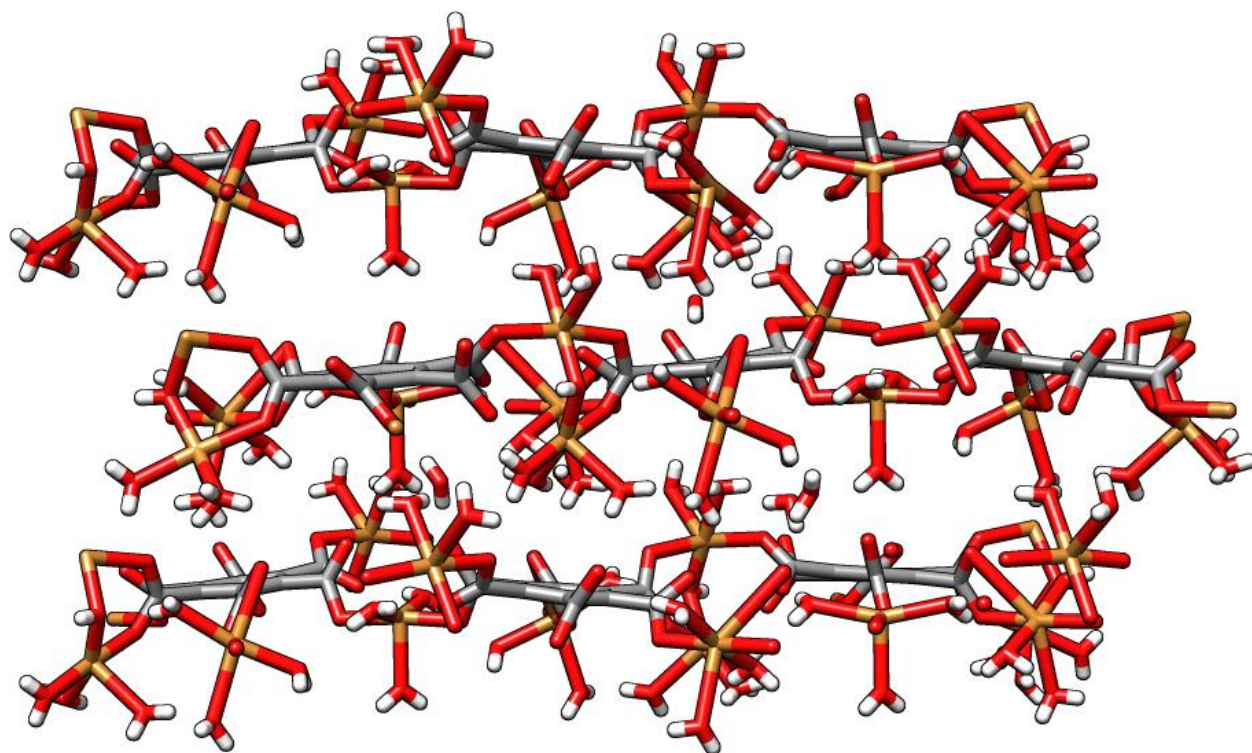


Figure 10. A side view (along the *a* axis, with the *b* axis horizontal) of three sheets of compound **5**, together with the intervening uncoordinated water molecules.

We believe that this structure represents a correction of a structure previously reported.<sup>20</sup> The chemical formula proposed by the authors of that report (doubled to give integer values) was  $[\text{Cu}_7(\text{Hmel})_2(\text{OH})_4(\text{OH}_2)_{17}] \cdot 9\text{H}_2\text{O}$  (it, and the compound name, are incorrectly given in the CSD with refcode VAPLED). H atoms appear not to have been experimentally located, at least not unambiguously, in the earlier experiment; the uncoordinated carboxylate group of the mellitate is represented as protonated, and disorder is proposed as an explanation of the near-equality of its C–O bonds. Our own interpretation of the structure requires no disorder and is based on H atoms that were refined with restraints, starting from positions found in a difference electron density map.



This structure combines some of the features of compounds **5** (a copper compound) and **4** (a compound including potassium). In common with compound **5**, the copper ions have a square-based pyramidal coordination geometry, with a long bond to water in the apical site. Both copper ions in this structure have three aqua ligands and are coordinated by two monodentate carboxylate groups from different mellitate anions; the minor difference between them is that all three aqua ligands on Cu2 are terminal, but one of the three on Cu1 (O13) forms a bridge to a potassium ion (a symmetry-equivalent of K2). Three carboxylate groups of the mellitate anion (at C1, C2, C3 and C5) coordinate to copper ions. The copper and mellitate ions together form a 2D polymer sheet structure (Figure 12).

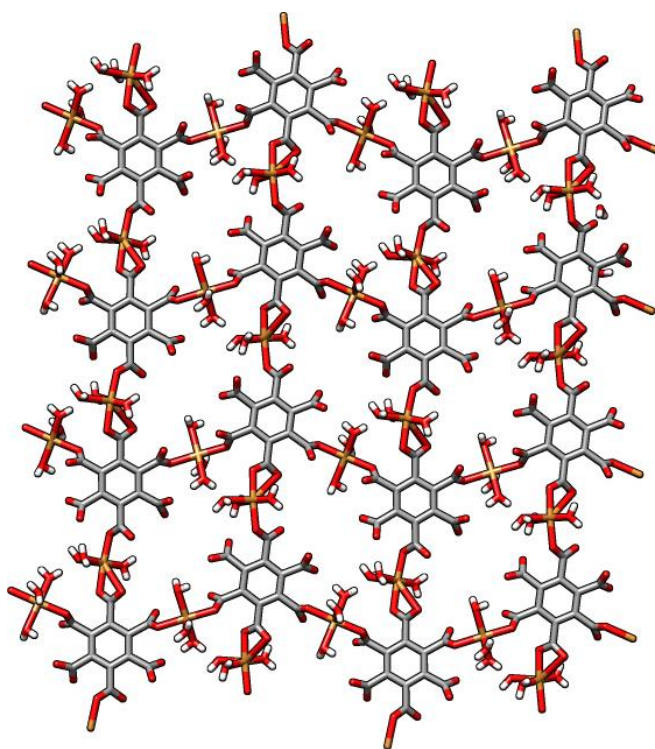


Figure **12**. The sheet polymeric structure of the copper and mellitate ions in compound **6**. Aqua ligands on copper are also included. The view direction is along the *b* axis, and the *a* axis runs horizontal.



The two potassium ions are both seven-coordinate. K1 is coordinated by two carboxylate groups, one of them monodentate and the other chelating, and by four terminally bound water molecules. K2, by contrast, is coordinated by two adjacent (ortho) carboxylate groups of one mellitate, two different ortho-carboxylate groups of another mellitate, two terminally bound water molecules, and a water molecule acting as a bridge to a copper ion. These coordinative interactions with potassium ions link the copper–mellitate sheets into a 3D network, which is further supported by hydrogen bonding involving the carboxylates, coordinated and uncoordinated water molecules.

**Compound 7.** The ingredients here were essentially the same as for compound **6** (but with sodium instead of potassium hydroxide), but the procedure was different, employing a silica gel impregnated with the hydroxide as the reaction medium into which the copper salt and mellitic acid diffused slowly. The product contains neither sodium nor hydroxide ions, and consists entirely of copper ions, coordinated and uncoordinated water molecules, and mellitate anions that here retain one of the acid protons and occur as  $\text{Hmel}^{5-}$ . This almost completely deprotonated mellitate is much less common than the fully deprotonated  $\text{mel}^{6-}$ , being reported previously in only two transition metal complexes: one of these is the copper compound discussed above, for which the  $\text{Hmel}^{5-}$  formulation is probably incorrect, and the other is a manganese compound supposedly containing also the only reported occurrence of the  $\text{H}_3\text{mel}^{3-}$  ligand,  $[\text{Mn}_4(\text{Hmel})(\text{H}_3\text{mel})(2,2'\text{-bipy})_4(\text{OH}_2)_8]$ .<sup>14</sup> Closer inspection of this structure and its deposited CIF indicates that there is a short  $\text{O-H}\cdots\text{O}$  hydrogen bond between a carboxylic acid group of  $\text{H}_3\text{mel}^{3-}$  and a carboxylate group of  $\text{Hmel}^{5-}$ , with an  $\text{O}\cdots\text{O}$  distance of 2.457 Å; this H atom has been positioned geometrically and refined with riding-model constraints. Transfer of the H atom to the putative carboxylate group, converting the  $\text{O-H}\cdots\text{O}$  arrangement to  $\text{O}\cdots\text{H-O}$ , would

probably fit the data just as well and would give the formula  $[\text{Mn}_2(\text{H}_2\text{mel})(2,2'\text{-bipy})_2(\text{OH}_2)_4]$ , very similar to another compound in the same publication in which 1,10-phenanthroline replaces 2,2'-bipyridyl and there is less water,  $[\text{Mn}_2(\text{H}_2\text{mel})(\text{phen})_2(\text{OH}_2)_2]$ . Indeed, the text of this publication describes both compounds as containing  $\text{H}_2\text{mel}^{4-}$  ligands, and these have been found in several other previously reported transition metal mellitate complexes.<sup>14,17,21,22</sup> as well as in some salts.<sup>23,24,25</sup> We believe, then, that the occurrence of  $\text{Hmel}^{5-}$  in compound **7** is unprecedented in any transition metal complexes of mellitic acid with a single intriguing exception discussed in detail below, although it has been reported in its cesium salt (H atom not located but assumed to be present either on a carboxylate group or on a water molecule),<sup>26</sup> and in one organic salt.<sup>27</sup>

The asymmetric unit of compound **7** contains two copper–mellitate–aqua assemblies that are not directly connected to each other; they are shown separately in Figures 13 and 14, a single representation being too congested for clarity.

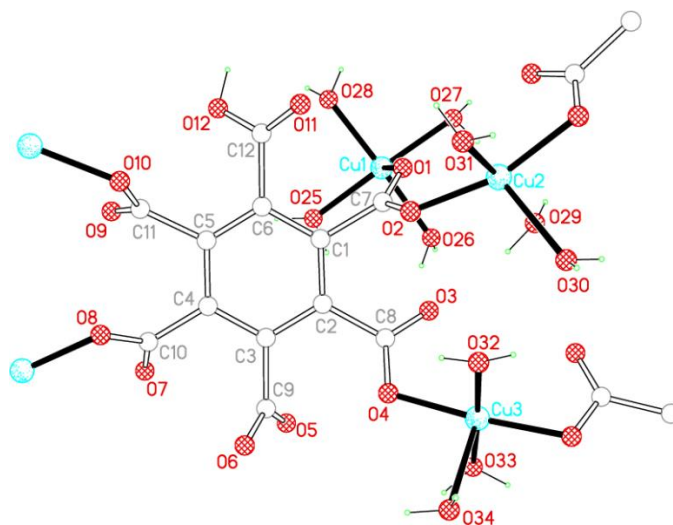


Figure **13**. The section of the asymmetric unit of compound **7** containing Cu1, Cu2 and Cu3 (with atom labels) together with additional atoms to complete the coordination environment.



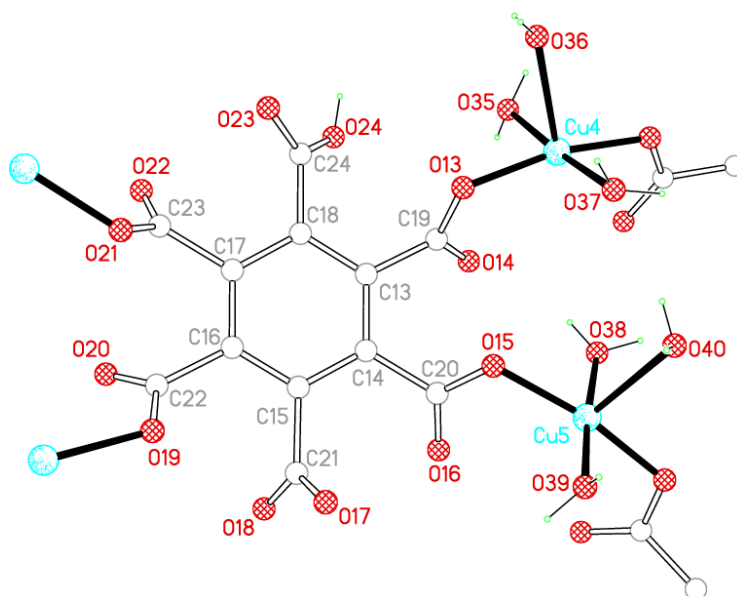


Figure 14. The section of the asymmetric unit of compound 7 containing Cu4 and Cu5 (with atom labels) together with additional atoms to complete the coordination environment.

As can be seen in these Figures, the two assemblies are very similar except for the inclusion of an extra  $\text{Cu}(\text{OH}_2)_4$  unit in the first one (Figure 13). The compound may thus be formulated as  $[\text{Cu}_3(\text{OH}_2)_{10}(\text{Hmel})][\text{Cu}_2(\text{OH}_2)_6(\text{Hmel})] \cdot 7\text{H}_2\text{O}$ . All aqua ligands in this structure are terminal, and all copper ions have a square-based pyramidal coordination with a long Cu–O apical bond. For Cu1 the apical position is occupied by a carboxylate group, and the basal plane contains four aqua ligands; the other four copper ions have an apical aqua ligand and two carboxylate groups opposite each other in the basal plane. Cu1 is therefore connected terminally to only one mellitate ligand, while each of the other copper ions connects two mellitates to form a 2D polymeric sheet structure; one sheet (containing Cu4 and Cu5) has all its mellitate benzene rings approximately coplanar, with the copper ions lying approximately in a parallel plane displaced to one side of this, while the other sheet (containing Cu2 and Cu3) has a very similar structure but with  $\text{Cu}(\text{OH}_2)_4$  units (Cu1) protruding on the opposite side from the displaced Cu2 and Cu3 atoms. This second sheet is shown in Figure 15.

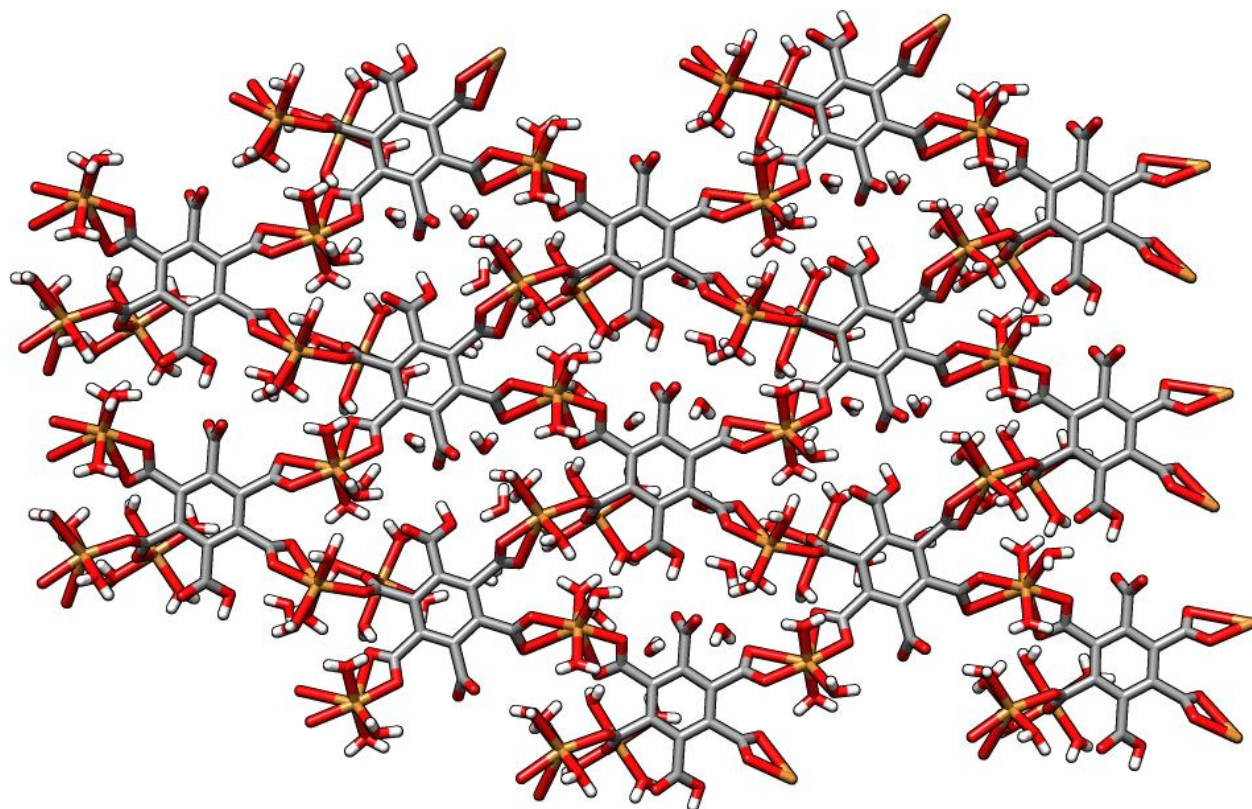


Figure 15. The CuI-containing polymeric sheet of compound **7**, together with uncoordinated water molecules. The view direction is approximately along [101] with the *b* axis running vertical.

H atoms in this structure were assigned partly from a difference electron density map and partly to generate a self-consistent hydrogen-bonding pattern. In particular, the H atom on one carboxylate group of each  $\text{Hmel}^{5-}$  anion (which is required for charge balance) was located in the difference map, attached to an O atom with a long C–O bond in an uncoordinated group, and was refined with a restrained O–H distance of 0.84 Å (along with the H atoms of the water molecules) but with no restraint on the orientation of the O–H bond. Both such carboxylic acid groups (one at C6 and one at C18) form hydrogen bonds with an uncoordinated carboxylate group having more nearly equal C–O bond lengths (in a symmetry-related mellitate in the same

polymer sheet). These features give us confidence that the  $\text{Hmel}^{5-}$  formulation and the location of the acid H atom are correct.

The two types of sheet are stacked alternately along the crystallographic  $a$  axis, with uncoordinated water molecules lying in spaces between the sheets, as shown in Figure 16.

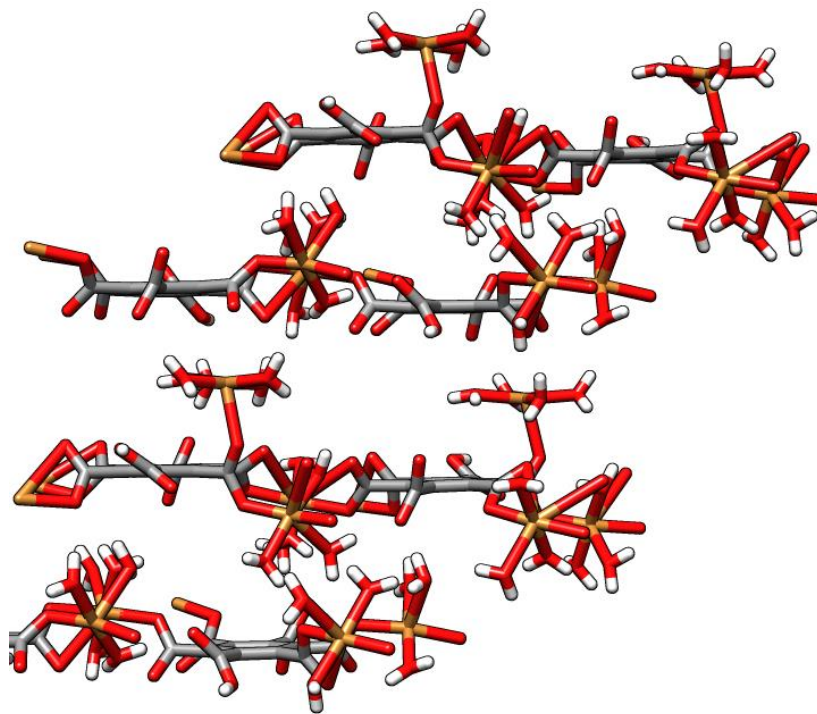


Figure 16. The stacking sequence of polymer sheets in compound **7**, viewed along the  $b$  axis, with the  $c$  axis running horizontal.

This structure is very similar to one previously reported as  $[\text{Cu}_4(\text{OH}_2)_{12}(\text{Hmel})_2\text{Cu}(\text{OH})_4] \cdot 6\text{H}_2\text{O}$ , which gives the same overall formula as compound **7** except for having 6 rather than 7 uncoordinated water molecules;<sup>28</sup> we note, however, that some of the water molecules (as well as one copper ion) were refined with disorder over partially occupied sites, so the precise water content may not be definitive. H atoms were not located in this structure, but a convincing case is made for the protonation of one specific carboxylate group on each of the two independent

mellitate anions on geometrical grounds. At a cursory glance the two structures appear to be essentially the same: transformation of the unit cell of compound **7** from space group *Cc* to the alternative *Ia* used in the previous report (refcode VUGBUU in the CSD) gives virtually identical values for two axis lengths, a 0.6 Å longer third axis for compound **7**, and a 10° difference in the monoclinic  $\beta$  angle. There is, however, a significant difference, revealed in Figure 17. The copper ion in VUGBUU equivalent to Cu1 in compound **7** does not belong exclusively to one sheet, but is connected to both sheets by long Cu–O(mellitate) bonds in an elongated and angularly distorted octahedral coordination geometry. This structure is thus still a 2D coordination polymer, but consists of double copper–mellitate sheets enclosing Cu(OH<sub>2</sub>)<sub>4</sub> links.

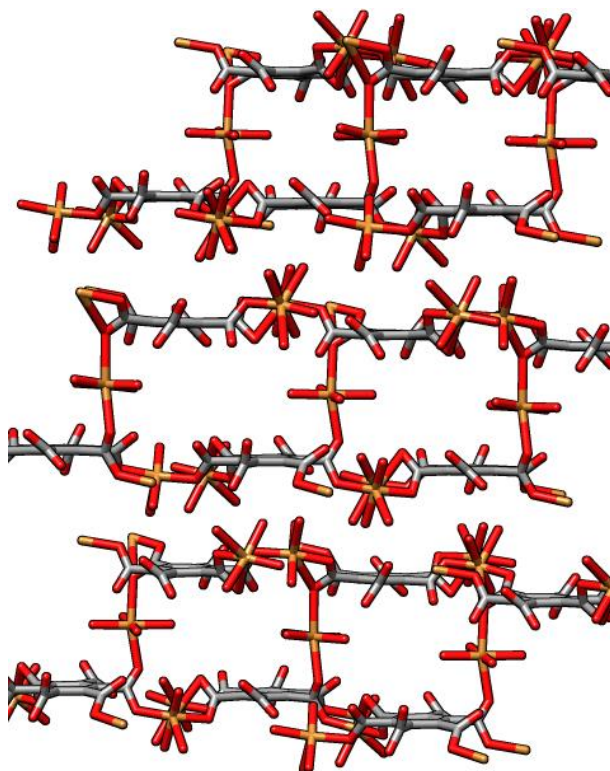


Figure 17. The stacking sequence of polymer sheets in the structure VUGBUU, viewed along the *b* axis.

The shortest Cu1...O(mellitate) contact in compound **7**, corresponding to the extra Cu–O bond in VUGBUU, is 2.818(7) Å to O16, with an O16...Cu–O angle of 150.6(2)°; this is much longer than the other Cu1–O bonds [1.953(7)–1.959(6) Å to aqua ligands and 2.214(6) Å to mellitate O1], and contrasts with the geometry in VUGBUU, where the two Cu–O(mellitate) bond lengths are 2.323 and 2.505 Å (with an O–Cu–O trans angle of 166.2°) and the bond lengths to aqua ligands are 1.949–2.058 Å.

These two structures are thus subtly but significantly different and demonstrate the complexities that can be encountered in this area of chemistry. As a further illustration, the compound [Cu<sub>3</sub>(OH<sub>2</sub>)<sub>12</sub>(mel)]·2H<sub>2</sub>O has a structure consisting of sheets similar to the Cu1-containing sheets of compound **7** arranged centrosymmetrically face-to-face so that the protruding Cu(OH<sub>2</sub>)<sub>4</sub> units are interleaved, and each forms a Cu...O(mellitate) contact of 2.729 Å with the partner sheet opposite the Cu–O(mellitate) bond of 2.308 Å, a geometry intermediate between those found in compound **7** and in VUGBUU.<sup>29</sup> By contrast, the compound [Cu<sub>3</sub>(OH<sub>2</sub>)<sub>3</sub>(mel)]·H<sub>2</sub>O, with a much lower water content, has a 3D coordination network, though the details of this structure are obscured by disorder.<sup>30</sup>

**Compound 8.** This is the only compound in this series in which we have introduced an auxiliary nitrogen-donor ligand, 4,4'-bipyridyl. Structures of a few transition metal mellitate complexes with 2,2'- and 4,4'-bipyridyl have previously been reported.<sup>14,22,31</sup>

The compound is formulated as [ $\{\text{Cu}(\text{OH}_2)(\text{EtOH})(4,4'\text{-bipy})\}_2(\text{H}_2\text{mel})$ ]. The asymmetric unit contains half of this formula and is shown in Figure 18, with its environment as in other Figures.

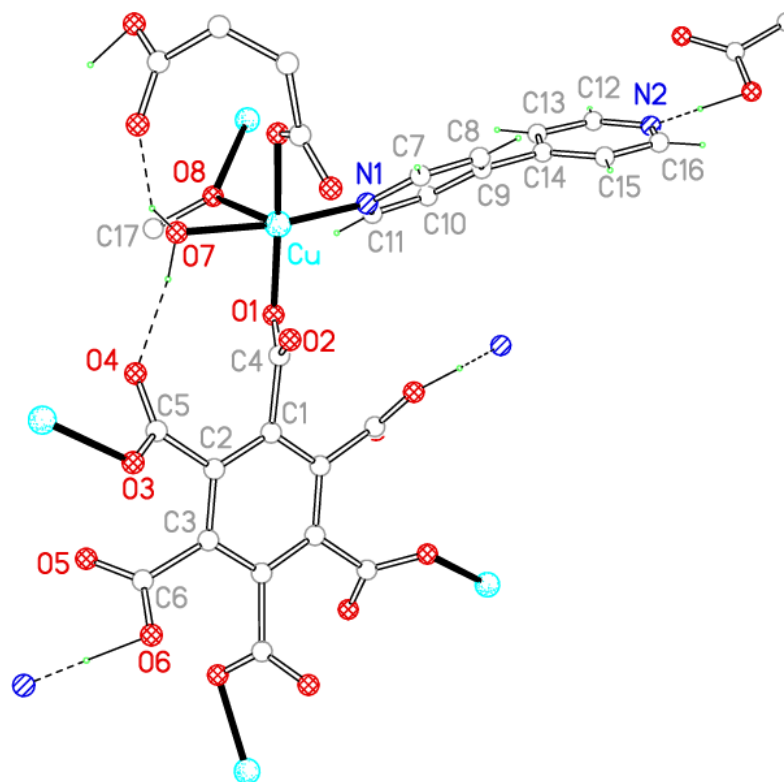


Figure 18. The asymmetric unit of compound **8**, together with the second half of the  $\text{H}_2\text{mel}^{4-}$  ligand and the coordination and hydrogen-bonding environment. Atoms of the asymmetric unit are labeled.

The mellitate anion retains two acid H atoms on opposite carboxylate groups. The anion lies on a crystallographic twofold rotation axis, which runs perpendicular to the benzene ring. Each of the deprotonated carboxylate groups coordinates a copper ion in monodentate fashion. The unique copper ion has a square-based pyramidal coordination with two carboxylate groups, a 4,4'-bipy N atom and a terminal water molecule in the basal sites, and a long apical bond to a methanol molecule, which lies on a twofold rotation axis and serves as a bridge between two copper ions. The methanol molecule displays high atomic displacements and may be disordered over its site, though this disorder has not been resolved; in any case, the methanol H atoms must be disordered and they have not been included in the structural model. While one N atom of the



4,4'-bipyridyl molecule is coordinated to Cu, the other serves as acceptor in a strong hydrogen bond from a carboxylic acid group [ $O \cdots N = 2.553(7) \text{ \AA}$ ]; this H atom was freely refined, and it is located essentially half-way between the O and N atoms [at  $1.31(5)$  and  $1.24(5) \text{ \AA}$  respectively]. The two rings of the 4,4'-bipyridyl molecule are twisted out of coplanarity by  $31.7^\circ$ .

The copper and mellitate ions form a 3D coordination network further supported by the bridging methanol molecules. This network has substantial hexagonal channels perpendicular to the  $c$  axis, which contain the 4,4'-bipy ligands, coordinating to Cu at one end and hydrogen-bonded to mellitate at the other, thereby extending across the channels (Figure 19).

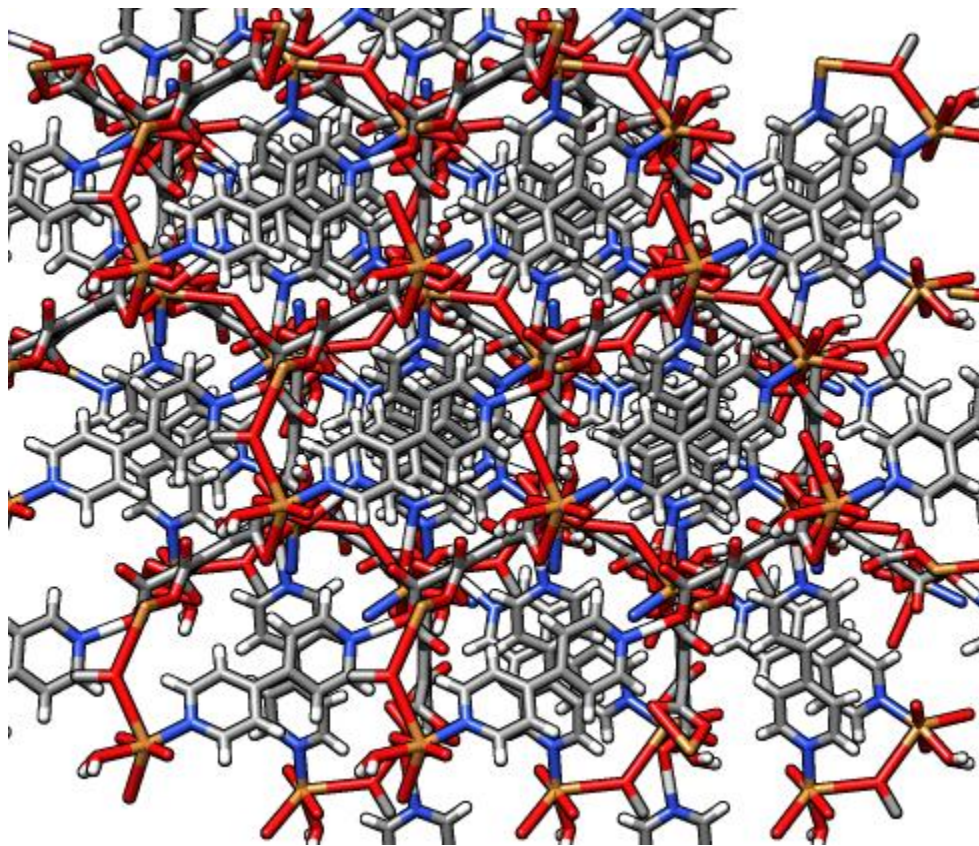


Figure 19. The 4,4'-bipy-filled hexagonal channel structure of compound **8**, viewed along the *c* axis.

The structural function of 4,4'-bipyridyl in this compound is quite different from that in previously reported mellitate complexes. In  $[M_2(OH_2)_6(H_2mel)(4,4'-bipy)] \cdot 0.33H_2O$  ( $M = Co$  or  $Ni$ ) it plays its more usual role as a linking ligand coordinated to two metal ions, and thereby connects metal–mellitate 1D chain polymers to form two interpenetrating 3D networks.<sup>22</sup> In  $[Cu(OH_2)_4(4,4'-bipy)]^{2+}[Cu_2(OH_2)_2(mel)(4,4'-bipy)]^{2-}$ , in stark contrast, copper–mellitate 1D polymer chains are cross-linked by 4,4'-bipy ligands and by hydrogen bonds to form double-stranded helical tubes with an overall negative charge, with polymeric 4,4'-bipy-linked  $Cu(OH_2)_4^{2+}$  cations as guests.<sup>31</sup>

## CONCLUSION

With eight compounds (seven of them new), together with comparisons with previously reported ones, we have demonstrated a wide variety of structural features. The main ingredients in these compounds are late first-row transition metal ions, mellitate anions (in most cases fully deprotonated), and both coordinated and uncoordinated water molecules. Further ionic species may be present in the products (alkali metals and/or hydroxide) depending on the pH conditions of the reagent solutions, and neutral ligands can also be deliberately introduced. Relatively small differences in reagents and conditions can lead to drastic changes in structure and composition, or to quite subtle but significant differences. Some general principles emerge from the structural comparisons: hydrothermal syntheses tend to generate products with a lower water content and denser structures; coordination geometry preferences for the various metal ions are largely constant – octahedral for  $Co^{2+}$  and  $Ni^{2+}$ , square-based pyramidal for  $Cu^{2+}$  with the possibility of



further secondary coordination to give approximately an elongated octahedral geometry; aqua ligands are usually terminal for transition metal ions, though they can serve as bridges if one or both of the cations are alkali metals, while hydroxide serves more readily as a bridging ligand; rotation of carboxylate groups markedly out of the benzene ring plane of mellitate, a necessary consequence of steric interactions, prevents ring-stacking from being a structural feature; extensive hydrogen bonding tends to make use of all available donors, which are mainly the coordinated and uncoordinated water molecules, and usually link the coordination polymer units into an overall 3D network whatever the dimensionality of these metal–mellitate polymers (1D, 2D or 3D).

However, the geometrical flexibility afforded by the degree of free rotation of carboxylate groups about the C–C bonds joining them to the benzene ring, together with the multitude of known carboxylate modes of coordination to metal centers, ranging from simple monodentate, through chelating, to bridging of two or more metal ions, makes the structural behavior of the mellitate anion rather unpredictable and very variable, compounded by the possibility, occasionally realized, of leaving one or more carboxylate groups protonated. This is in contrast, for example, with the widely used terephthalate anion (benzene-1,4-dicarboxylate), for which it is normal for the carboxylate groups to lie essentially in the ring plane, giving a totally planar ligand. Mellitic acid, we may conclude, does not lend itself well to a design approach in its coordination chemistry, in which serendipity plays a significant role.

## ASSOCIATED CONTENT

### **Supporting Information.**

Full crystallographic details for complexes **1–8** in cif format and in conventional tabulated form together with displacement ellipsoid plots; observed and calculated powder X-ray diffraction patterns. This material is available free of charge via the Internet at <http://pubs.acs.org>. CCDC numbers 1009817–1009824 contain the supplementary crystallographic data. These data can also be obtained free of charge, upon request, at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax (Internet) +44–1223/336–033; e-mail [request@ccdc.cam.ac.uk](mailto:request@ccdc.cam.ac.uk)].

#### AUTHOR INFORMATION

##### **Corresponding Author**

\*email [bill.clegg@ncl.ac.uk](mailto:bill.clegg@ncl.ac.uk)

##### **Present addresses**

†Present address: Department of Chemistry, Northwestern University , Evanston, IL 60208, USA

##### **Author Contributions**

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##### **Notes**

The authors declare no competing financial interest.

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